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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in Composition of Matter and use thereof

We, UNITED STATES RUBBER COMPANY, of Rockefeller Center, 1230, Avenue of the Americas, New York, State of New York, United States of America, a Corporation organized and existing under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composition and to an article of manufacture embodying a glass base member and the said composition in cured form and the method of making such an article of manufacture. More specifically, the invention relates to a method of making resin-bonded, glass fibre articles in which the bonding of the resin to the glass is substantially improved.

For many applications it is desirable to intermix glass fibres with resins. The advantages to be gained from the incorporation of the fibres are increases in the tensile, compression, flexural, and impact strengths of the resins. The improvement in these properties is roughly proportional to the amount of glass fibre incorporated in the resin; since high glass fibre contents per unit volume are most readily obtained by the use of glass fibre mats or woven glass fabrics, reinforcement with these compositions is the preferred method of obtaining maximum strength properties.

It is well known to those active in this field that the flexural strength, and other physical properties of resin-bonded, glass fibre constructions, particularly glass fibre laminates, are increased by tighter bonding between the resin and the glass. The methods heretofore developed for improving the bonding have involved treating the glass fibres with agents which form a film on the glass, this film being bonded strongly to the glass and having reactive double bonds which are capable of combining chemically with the resin during cure.

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It has previously been proposed to apply to the glass fabric a bonding agent known as "Volan" (Registered Trade Mark). This chemical is a Werner type compound in which methacrylic acid is coordinated with chromium. It may be described as methacrylateochromium (III) chloride. This material is not as effective as the treating agents of our invention.

More recently, (See Bjorksten *et al.*, Modern Plastics, July 1952, pages 124 and 188) it has been shown that treatment of glass fibres with vinyltrichlorosilane, or with a mixture of vinyltrichlorosilane and beta-chloroallyl alcohol, causes a modification of the surface of the fibres thereby enabling them to bond more strongly to polyester resins.

Treatment of glass fibres with vinyltrichlorosilane or mixtures thereof with beta-chloroallyl alcohol is objectionable in that hydrogen chloride is evolved as a product of the reaction. Hydrogen chloride is a health hazard and is exceedingly harmful to the equipment used in textile finishing operations. The same objections apply if such material are added to the resin, and in addition the product is seriously impaired, the glass laminate being wholly unacceptable.

Other workers have developed a method for treating glass fibres which involves the use of sodium salt of vinylsiloxanol. This salt may be prepared by reacting vinyltrichlorosilane with an aqueous solution of sodium hydroxide. The objection to this method of treatment is that the sodium chloride and excess alkali contained in the treating agent are difficult to remove and therefore make the treatment an expensive operation.

Other workers have employed solutions of polyvinyl siloxanes in toluene in conjunction with amine catalysts such as triethanolamine to modify the surfaces of glass fibres. However, this method is objectionable in that the solvent, toluene, must be completely removed and thereafter the fabric must be subjected to very

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high temperatures (at least 500° F.) to complete the modifying reaction.

The principal object of our invention is to provide a simple, economical and commercially feasible method of bonding polyester resins to glass, particularly glass fibre, which method obviates the objections to previous methods such as are described above.

We have now discovered that certain organo-
10 organoxysilanes, when added to curable polyester resins in small amounts, impart a substantial strengthening of the bond that may be obtained between said resins and glass. The use of the organoorganoxysilanes in the process
15 of our invention causes a particularly great improvement in the resin-glass bond after ageing under high humidity conditions. Moreover, the method of our invention offer marked practical advantages over the methods heretofore employed for the same purpose. The particular
20 organoorganoxysilanes which may be used in our invention are those selected from the group consisting of vinylalkoxysilanes, vinyl-2-chloroalkoxysilanes, vinylallyloxysilanes, vinylacyloxysilanes, and products of the reaction of
25 vinylchlorosilanes with saturated aliphatic, dihydric alcohols.

The silane additives of our invention are generally prepared by reacting a vinylhalosilane
30 with the appropriate alcohol or organic acid. This reaction is effected by merely commingling the two reactants under such conditions that they react with the liberation of hydrogen halide. The silane additives referred to as the
35 products of reaction of vinylchlorosilanes with saturated, aliphatic, dihydric alcohols are prepared according to the process set out in our Specification No. 710,051. According to this process the reactants are combined in such
40 proportions that the ratio of alcoholic hydroxyl groups to chlorine atoms in the initial reaction mixture is greater than unity.

Our silane additives may have from one to three vinyl groups linked directly to the silicon
45 and from one to three hydrocarbon chains linked to the silicon through an oxygen atom. We prefer to use those silanes in which there is one vinyl group linked directly to the silicon, the remaining valences of the silicon being
50 occupied by alkoxy, 2-chloroalkoxy-, allyloxy-, or acyloxy groups. The alkoxy, 2-chloroalkoxy and acyloxy groups contain from 2 to 6 carbon atoms.

The following silanes are illustrative of the chemical additives falling within the scope of our invention:—

- Vinyltriethoxysilane
- Vinyltripropoxysilane
- Vinyltributoxysilane
- 60 Divinyldiethoxysilane
- Trivinylethoxysilane
- Vinyltriallyloxysilane
- Vinyltris-(2-chloroethoxy)silane
- Vinyltris-(2-chloropropoxy)silane
- 65 Divinylbis-(2-chloroethoxy)silane

Vinyltriacetoxysilane

The silane additives of our invention also include silanes formed by the reaction of a vinylchlorosilane with a saturated aliphatic dihydric alcohol, in which reaction the vinyl-
70 chlorosilane is vinyltrichlorosilane, divinyldichlorosilane or trivinylchlorosilane and the saturated aliphatic dihydric alcohol is ethylene glycol, propylene glycol, trimethylene glycol, diethylene glycol, triethylene glycol, or dipro-
75 pylene glycol.

The potentially curable resinous compositions with which the silanes of our invention are admixed are well-known materials and comprise an esterification product of an alpha-
80 ethylenic alpha, beta-dicarboxylic acid with a glycol, this esterification product being an advanced linear polyester containing unesterified carboxyl groups and having an acid number of from 5 to 100 and being dissolved in and
85 copolymerizable with a liquid monomeric polymerizable ethylenic compound which is immiscible with water, an organic peroxide being added as a polymerization catalyst shortly before the co-polymerization is to be effected.
90 Polyesters of this type are described in U.S. Patent 2,195,362. In use, unsaturated linear polyesters of this type are mixed with a polymerizable monomer, for instance styrene,
95 diallyl phthalate or triallyl cyanurate, and the mixture is cured to solid form by heating in the presence of a suitable catalyst. Typical resinoid mixes of unsaturated linear polyester and copolymerizable monomer used in practicing
100 our invention are described in U.S. Patent 2,255,313 and in British Patents 540,168 and 540,169. As descriptive of such mixes, the disclosure of said patents is hereby incorporated by reference in order to avoid undue repetition.
105 As is well known the unsaturated dicarboxylic acid may be partially replaced by another dibasic acid which may be typified by adipic acid, succinic acid, sebacic acid, phthalic acid, and tetrachlorophthalic anhydride, and which may
110 be used in amounts up to 3 moles per mole of unsaturated dicarboxylic acid.

Any organic peroxide that functions as a free radical type polymerization initiator is operable in our invention. Examples of such peroxides
115 are hydroperoxides, e.g., tertiary-butylhydroperoxide, cumene hydroperoxide, para-methanehydroperoxide, etc.; peroxy esters, e.g., di-*t*-butyl diperoxyphthalate, *t*-butyl peroxyacetate, etc.; alkyl peroxides, e.g., di-*t*-butyl peroxide, dibenzyl peroxide, etc.; ketone
120 peroxides, e.g., methylethyl ketone peroxide, cyclohexanone peroxide, etc.; and acyl peroxides, e.g., benzoyl peroxide, para-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, lauroyl peroxide, etc.
125

Probably the most important application of our invention is its use in bonding fibrous glass to cured polyester resins of the above type. The advantages obtained by this application of our invention are increases in the tensile, com-
130

pression and flexural strength of the products, and particularly greater strength retention after the products have been exposed to water. The compositions also have greater transparency when prepared according to our invention.

Our method of improving the resin-to-glass bonding provides economy because it embodies the step of adding a chemical to the resin and therefore is much easier to carry out than the prior art processes which embody the steps of uniformly coating glass fibres with treating agent, washing, high-temperature curing of the treating agent on the fibres, etc. Our invention permits more flexibility for the fabricator, since he can readily adjust the extent of his treatment to the requirements of each particular job. In addition, our invention obviates the complicated equipment and steps required for pretreatment of the glass fibres.

Suitable amounts of the silane additives used in the practice of our invention vary widely, depending upon many factors. Generally speaking, however, the amount will range from 0.1 to 10% of the weight of the copolymerizable mixture of linear polyester and monomer. We prefer to employ from 0.5 to 2% of a vinylhalosilane-diol reaction product.

The surface of the glass should be clean, i.e., it should be free from any extraneous material which would adversely affect the bonding of the resin thereto. In particular, it should be free from organic material which would adversely affect the degree of bonding, especially those organic materials which are applied to glass fibre during manufacture for various purposes such as for lubricating the fibres or sizing them.

The maximum effectiveness of the silane additives is obtained when well cleaned glass fibres are used. If a sizing has been applied to glass fibres, it may be removed by heating them to temperatures within the range of 600° to 900° F. It is well known to those skilled in the art that cleaning may be effected at these temperatures either by continuous methods requiring only a few minutes or by batch methods requiring from 24 to 72 hours.

The following example illustrates that our invention is very useful in securing adhesion of curable alkyd resin finishes to glass surfaces. More particularly, the example demonstrates how polyester resin can be bonded to a glass plate by the method of our invention.

EXAMPLE I.

The silane additive used in this experiment is the reaction product of vinyltrichlorosilane and diethylene glycol. This reaction product is prepared by placing 225 parts of diethylene glycol in a vessel and adding 150 parts of vinyltrichlorosilane thereto with stirring. During addition of the silane, hydrogen chloride is evolved. The reaction mixture is then heated to 200° C. and held at this temperature for 2—3 hours. The final product contains essentially no hydrolyzable chlorine.

Ninety-eight parts of maleic anhydride, 148 parts of phthalic anhydride, and 163 parts of propylene glycol are heated for 3 hours at 200° C., the final half-hour being at reduced pressure. The resultant alkyd resin has an acid number of 55. Sixty-seven parts of this alkyd are combined with 33 parts of styrene and 1.5 parts benzoyl peroxide to form a curable liquid casting resin. This resin is designated Resin I.

Approximately 5 grams of Resin I, to which has been added 2% of the reaction product of diethylene glycol and vinyltrichlorosilane, and 1.5% of benzoyl peroxide, are poured onto a glass plate, allowed to flow out to a film, and cured under an infrared lamp. Simultaneously a 5-gram portion of the resin catalyzed with 1.5% benzoyl peroxide, but containing no silane reaction product, is cured on the same glass plate. After the cure has been completed the resin films are cracked by thermal shock. Observation shows the film of resin containing the silane reaction product to have attached to it portions of glass which have been pulled from the glass plate, whereas the film of resin containing no silane comes away from the glass cleanly and smoothly.

In demonstrating the effect of our invention on glass-fibre-reinforced polyester compositions, we have chosen to report the flexural strength of moulded flat sheets of the compositions. It is well known to those experienced in the field that changes in tensile strength and compressive strength generally parallel changes in flexural strength. Our flexural strength data have been obtained as recommended in Federal Spec. L—P—406a-Method 1031.

The most significant improvement in the reinforced polyester compositions brought about by the method of our invention is greater strength retention after ageing in water. As is common practice among those experienced in the field, we have measured this property by determining the flexural strength of the compositions before and after they have been immersed in boiling water for 3 hours. This ageing treatment is generally recognized to be equivalent to standing at least one month in water at room temperature.

EXAMPLE II.

This example demonstrates the use of the glycol-silane reaction product to make resin-bonded glass fabric laminates of high flexural strength.

Two different polyester resins are used: one is the same as that used in Example I, i.e., Resin I; the second is prepared as follows:—

Eighty-eight parts of maleic anhydride, 148 parts of phthalic anhydride, 29 parts of tetrachlorophthalic anhydride, and 130 parts of ethylene glycol are heated about 4 hours at 220° C. The alkyd so prepared has an acid number of 40. Seventy parts of this alkyd are combined with 30 parts of styrene and 1.5 parts of benzoyl peroxide to form a curable

liquid resin. This resin is designated Resin II.

The additive used is the same glycol-silane reaction product that was used in Example I. It is intimately incorporated with the curable liquid resin mixture before it is brought into contact with the glass fabric.

Laminates of glass fabric and polyester resin are made up containing 12 plies of glass fabric. The glass fabric used in these constructions is a long-shaft satin weave fabric with 225-1/3 warp, 225-1/3 fill, and 57 warp ends with 54 picks. The glass fabric has been cleaned by heating at 750° F. for 48 hours. The total

thickness of each laminate is about 0.125 inch, and the glass content is about 64% by weight. One and one-half per cent of benzoyl peroxide is used as a catalyst for curing the resin. The laminates are cured for approximately 15 minutes at 160° F. followed by 15 minutes at 250° F. Two laminates are made with each resin; the resin used in one of the laminates contains an addition of 2% of the reaction product; the resin used in the other laminate is not modified. Results are summarized in the following table.

TABLE I.

Type of resin	% silane additive added to resin	Flexural strength (psi)	
		Initial	After 3 hours in boiling water
30	I	63,900	49,000
	I	55,500	24,200
	II	58,000	51,500
	II	54,200	32,900

The data in Table I show that the silane additive imparts an improvement in the initial flexural strength of the laminates to which it has been added. The most pronounced effect of the silane additive, it will be observed, is the improvement in flexural strength retention after ageing in boiling water.

Silane additives which are reaction products of vinylchlorosilanes and other dihydric alcohols, besides diethylene glycol, improve the flexural strength of resin bonded, glass fabric laminates. Thus, for example, a laminate prepared with a resin containing the reaction product of vinyltrichlorosilane and propylene glycol has an initial flexural strength of 60,200 psi and a flexural strength, after three hours in boiling water, of 51,400 psi. A similar laminate containing no reaction product has a substantially lower initial flexural strength and lower flexural strength after 3 hours in boiling water.

The following example illustrates the preparation of laminates containing resins to which vinyltriethoxysilanes have been added.

EXAMPLE III.

Three resins are used to prepare the laminates of this example. The resins heretofore designated as Resins I and II are used as well as Resin III which is a mixture consisting of

70% of the product prepared according to the method of Example 1 of U.S. Patent 2,195,362 combined with 30% of diallyl phthalate monomer.

Two laminates are made from each resin. Two parts of vinyltriethoxysilane (per 100 parts of resin) are added to a portion of Resin I. Similarly, one part of vinyltriethoxysilane is added to a portion of Resin II and to a portion of Resin III. As controls, the resin used in the second laminate of each pair contains no silane additive.

One and one-quarter per cent of cumene hydroperoxide is added as a catalyst for curing Resins I and II; 1.5% of benzoyl peroxide is added as a catalyst for curing Resin III. The resin-impregnated laminates are cured by placing the uncured laminates in a press adjusted to a temperature of 100° F.; the temperature of the press is then raised to 300° F. over the course of 30 minutes, and held at 300° F. for 15 more minutes. A curing cycle of this type is adopted so as to insure that the resin will completely cure, regardless of the decomposition temperature of the peroxide. The decomposition temperatures of the peroxides used in the cure are below 300° F.

Flexural strength data are obtained on all of the laminates. The data are summarized in the following table.

TABLE II.

	Type of resin	Per cent. vinyltriethoxysilane	Flexural strength (psi)	
			Initial	After 3 hours in boiling water
5	I	none	38,600	17,900
	I	2%	58,700	52,200
	II	none	56,100	23,000
	II	1%	63,500	50,600
10	III	none	44,600	21,800
	III	1%	62,700	50,800

The flexural strength data in Table II illustrate that the presence of vinyltriethoxysilane in a variety of curable polyester casting resins imparts a substantial improvement in the flexural strength of glass fabric laminates containing these resins, particularly after they have been in boiling water for 3 hours.

EXAMPLE IV.

This example illustrates the use of vinyltri-

propoxysilane in the process of our invention. 20 A pair of laminates are prepared similarly to those in Example II. Resin I is used, and 2% of vinyltri-*n*-propoxysilane is added to a portion of it. Another portion of resin I, as a control, is unmodified. One and one-quarter per 25 cent of cumene hydroperoxide is added to each portion of resin, as the curing catalyst.

The flexural strength data for the two laminates are summarized in Table III.

TABLE III.

	Type of resin	Per cent. vinylpropoxysilane	Flexural strength	
			Initial	After 3 hours in boiling water
30	I	none	38,600	17,900
	I	2%	62,600	52,600

Comparison of the data given in Tables II and III shows that vinyltri-*n*-propoxysilane causes an improvement in flexural strength comparable to that obtained with vinyltriethoxysilane.

It is not believed that organoorganoxysilanes other than vinylorganoxysilanes will improve the flexural strength of laminates to the degree that vinylorganoxysilanes do. For example, our experience with the dihydric alcohol reaction products has shown that the products formed by the reaction of dihydric alcohols with cyclohexenyltrichlorosilane, diethylchlorosilane, and amyltrichlorosilane do not cause an improvement in the flexural strength of laminates comparable to that obtained with the reaction products of dihydric alcohols and vinylhalosilanes.

Allylorganoxysilanes may be considered as next higher homologues of the corresponding vinylorganoxysilanes. Of all the organo-

organoxysilanes, the behaviour of the allyl compounds might be expected to be the most closely comparable to that of vinylorganoxysilanes. The surprising thing is that even allylorganoxysilanes do not impart an improvement in flexural strength, particularly after the laminate has been placed in boiling water for 3 hours, of the same degree that is obtained with vinylorganoxysilanes. This is illustrated in the following example.

EXAMPLE V.

A pair of laminates were prepared similarly to those in Example II, with Resin I. One portion of the resin contained 1% of added allyltriethoxysilane; the other contained 1% of added vinyltriethoxysilane. One per cent. of di-*t*-butyl diperoxophthalate was added to each resin. Each laminate was press-cured for 15 minutes at 200° F., then for 30 minutes at 300° F. The flexural strength data for the cured laminates are summarized in Table IV.

TABLE IV.

Type of resin	Organo-alkoxysilane	Flexural strength	
		Initial	After 3 hours in boiling water
I	allyltriethoxysilane	58,000	40,300
	vinyltriethoxysilane	59,000	56,100

As is evident from Table IV, the flexural strength, after 3 hours in boiling water, of the laminates containing vinyltriethoxysilane is about 40% higher than that of the laminate containing allyltriethoxysilane.

EXAMPLE VI.

This example illustrates the use of vinyl-2-chloroalkoxysilanes, vinylallyloxysilanes, and vinylacyloxysilanes in the process of our invention to make resin-bonded, glass fabric laminates.

Resin II is used in the construction of the

laminates. The laminates are made from the same glass fabric that was employed in Example I. Cumene hydroperoxide (1.25%) is added as the curing catalyst. The resin-impregnated laminates are cured by placing the uncured laminates in a press adjusted to a temperature of 100° F.; the temperature of the press is then raised to 300° F. over the course of 30 minutes, and held at 300° F. for 15 more minutes. The following table shows the physical data obtained on the various laminates thus prepared.

TABLE V.

Silane additives	Parts silane	Flexural strength	
		Initial	After 3 hours in boiling water
Vinyltriacetoxysilane	2	56,600	49,200
Vinyltri-2-chloroethoxysilane	2	60,400	53,200
Vinyltriallyloxysilane	2	55,900	51,300
None (control)	0	48,200	32,300

The data in Table V show that when resins containing a vinylacyloxysilane, a vinyl-2-chloroalkoxysilane, or a vinylallyloxysilane, is used in making glass fabric laminates, the initial flexural strength of the cured laminates is substantially higher than that of a laminate made with a resin containing no silane additive. The data also show that a similar but more marked difference exists between the two classes of laminates after they have been aged for three hours in boiling water. Comparison of the data in Table V with the data in Tables I through IV shows that the level of improvement in flexural strength imparted by our silane additives is about the same, regardless of the particular silane additive actually used.

As heretofore stated, only relatively small

amounts of our silane additives are required. In the following example it is demonstrated that with amounts of the silane additives as low as 0.5%, very significant improvements in the strength of the laminate are obtained.

EXAMPLE VII.

A series of laminates containing different amounts of vinyltriethoxysilane were prepared in a manner similar to those in Example II. Resin I, to which 1.25% of cumene hydroperoxide was added, was used in each laminate. The curing cycle was the same as that in Example III. The exact composition of the several laminates, and the flexural strength data obtained, are shown in Table IV.

TABLE VI.

Type of resin	Per cent. vinyl triethoxysilane	Flexural strength	
		Initial	After 3 hours in boiling water
I	none	38,600	17,900
I	0.5	69,900	58,400
I	1	72,500	59,500
I	2	69,800	59,500
I	5	67,600	55,900

The ineffectiveness of using our silane additives in a composition containing a glass fabric from which the lubricant has not been removed, is demonstrated in Example VIII.

5 EXAMPLE VIII

Laminates are prepared similarly to those described in Example II except that the glass fabric used has not been given any cleaning treatment, and so is still sized with the lubricant employed in their preparation. This lubricant

is composed of a starch, vegetable oil, softener, gelatin, vinyl polymer and an emulsifying agent. For purpose of comparison, data on laminates containing heat-cleaned glass fabric (heated under such conditions as to remove all organic material therefrom) are also reported. The reaction product of vinyltrichlorosilane and diethylene glycol is used as the silane additive, and Resin I is employed in all of the laminates.

TABLE VII

	Fibre surface	Amount of silane additive	Flexural strength	
			Initial	After 3 hours in boiling water
25	Sized	none	35,800	24,700
	Sized	2%	35,000	21,500
	Heat cleaned	none	55,500	24,200
	Heat cleaned	2%	63,900	49,000

Our invention is applicable to the preparation of resin bonded, glass fibre structures regardless of the arrangement of the glass fibres in the structures. As has been demonstrated in the preceding examples, glass fabric laminates having improved flexural strength can be made by the process of our invention. Our invention may be applied equally well to improve the properties of polyester structures reinforced with randomly oriented, chopped glass fibres. For example, our invention can be advantageously used in improving polyester structures reinforced with a mechanically integrated glass fibre mat. Such a mat may be prepared by blowing chopped glass fibres onto a moving wire screen so that the fibres are randomly deposited on the screen. The fibres are then mechanically integrated by the action of many barbed needles which pierce the mat and in the return stroke carry a strand of glass fibre in loop form, from the top surface to the lower surface of the mat. The loops of glass fibres passing through the mat act to integrate the mat and give it a mechanically stable construction. The mechanical stability of the mat can be modified as desired by varying the number of barbed needles which pierce the mat.

Another type of mat construction that can be used in our invention is one in which the glass fibres are oriented in one direction. A conventional resin bonded structure made from such a mat has an initial flexural strength of 106,600 psi and a flexural strength after 3 hours in boiling water of 75,300 psi. The flexural strength is measured by bending at a right angle to the direction of fibre orientation. A similar structure containing the reaction product of vinyltrichlorosilane and diethylene glycol has an initial flexural strength of

121,900 psi and a flexural strength of 97,700 after 3 hours in boiling water. The improvement in flexural strength imparted by the silane is evident.

Another instance of the utility of our invention is in the improvement of moulding compositions of the type which consist primarily of polyester resins and short length glass fibres intermixed therein.

From the foregoing, those skilled in the art will appreciate that the present invention provides many advantages. The principal advantage is that a considerable improvement in the degree of adhesion of cured polyester-type resins to glass or the like is obtained by adding our silane additives to the resin prior to bringing it into contact with the glass or like surface followed by curing of the resin while contact is maintained. This process has the advantage of being much easier to carry out than a procedure in which the glass is pretreated with a treating agent. As indicated above, it makes for greater flexibility for the manufacturer. Another advantage is that the liberation of hydrogen halide in the plant where the glass or the like is coated or bonded with the resin is obviated. Numerous other advantages of our invention will be obvious to those skilled in the art.

What we claim is:—

1. A composition comprising an esterification product of an alpha-ethylenic alpha, beta-dicarboxylic acid with a glycol, said product being an advanced linear polyester containing unesterified carboxyl groups and having an acid number of from 5 to 100 and being miscible with and copolymerizable with the polymerizable ethylenic compound hereinafter mentioned to yield a solid resinous material, liquid polymerizable ethylenic monomer

- immiscible with water, and a silane selected from the group consisting of vinylalkoxysilanes and vinyl-2-chloroalkoxysilanes wherein each alkoxy group contains from 2 to 6 carbon atoms, vinylallyloxysilanes, vinylacyloxysilanes wherein the acyloxy group contains from 2 to 6 carbon atoms, and products of the reaction of vinylchlorosilanes with saturated aliphatic dihydric alcohols, said vinylchlorosilane and said alcohol having been interacted in such proportions that the ratio of alcoholic hydroxyl groups to chlorine atoms in the initial reaction mixture is greater than unity.
2. A composition as set forth in claim 1, wherein said silane is vinyltriethoxysilane.
3. A composition as set forth in claim 1, wherein said polymerizable monomer is styrene, and wherein said silane is vinyltriethoxysilane.
4. A composition as set forth in claim 1, wherein said polyester is the condensation product of maleic anhydride, phthalic anhydride and propylene glycol and wherein said polymerizable monomer is styrene and said silane is vinyltriethoxysilane.
5. An article of manufacture comprising a glass base and a composition as set forth in claim 1 integrally bonded thereto by curing with an organic peroxide.
6. A glass fibre-reinforced resin composition comprising glass fibres and a composition as set forth in claim 1, said composition having been cured with an organic peroxide.
7. A composition as set forth in claim 6 wherein the polymerizable monomer is styrene and said peroxide is a peroxy ester.
8. A composition as set forth in claim 6 wherein the polymerizable monomer is styrene and said peroxide is a hydroperoxide.
9. A composition as set forth in claim 6 wherein the polymerizable monomer is styrene and said peroxide is an alkyl peroxide.
10. A composition as set forth in claim 6 wherein the polymerizable monomer is diallyl phthalate and said peroxide is a peroxy ester.
11. A composition as set forth in claim 6 wherein the polymerizable monomer is diallyl phthalate and said peroxide is an acyl peroxide.
12. A glass fibre-reinforced resin composition comprising a glass fibre mat of randomly oriented glass fibres that are mechanically integrated, and a composition as set forth in claim 1, said composition having been cured with an organic peroxide.
13. A glass fibre-reinforced resin composition comprising multiple layers of glass fabric and a composition as set forth in claim 1, said composition having been cured with an organic peroxide.

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